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Fluorescence spectra of praseodymium and samarium amino acid ternary complexes

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Abstract : Fluorescence spectra of Pr^{3+} ternary complexes with L-alanine or L-cysteine as primary and 2–3 butandiol as secondary ligands have been recorded. One band for Pr^{3+} complexes and four bands for Sm^{3+} complexes have been observed. Their assignments have been given.

Keywords : Praseodymium ternary complexes, samarium ternary complexes and fluorescence spectra.

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1. Introduction

A comparative study of fluorescence of Pr^{3+} ion in state of glass, aqueous solution and powder was reported recently [1]. Though the absorption spectra of rare earth amino acid complexes have been studied [2-6], the data on their fluorescence spectra are very scanty. The present communication reported the fluorescence spectra of Pr^{3+} and Sm^{3+} amino acid ternary complexes in state of aqueous solution.

2. Experimental

The fluorescence spectra were recorded on Hitachi Fluorescence Spectrophotometer model "F-3000" in the visible region in triple distilled water. The complexes of Pr^{3+} and Sm^{3+} with amino acids (L-alanine [A] or L-cysteine [C] as primary ligand and 2,3-butandiol [BD] as secondary ligand in the molar ratio 1 : 1 : 1, 1 : 2 : 1 and 1 : 1 : 2 have been synthesized by well established method [7,5]. The chemicals used were of AR grade. Praseodymium and samarium chlorides (99.99% pure) were supplied by Indian Rare Earths Limited.

3. Results and discussion

The fluorescence spectra of twelve Pr^{3+} and Sm^{3+} ternary amino acid complexes have been recorded in the state of aqueous solution. Their spectra are given in Figures 1 and 2.

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Pr^{3+} complexes :

Pr^{3+} ions are known [8,9] to cause a strong concentration quenching and as such, it is extremely difficult to observe an appreciable fluorescence from Pr^{3+} complexes in aqueous solution. The fluorescence spectra of all the six Pr^{3+} complexes have been monitored at the excitation wavelength, $\lambda_{ex} = 445$ nm, which corresponds to the most intense absorption band $\left({}^3H_4 \rightarrow {}^3P_2\right)$ in their absorption spectra (Figure 1). The resulting spectra have been presented in Figure 1. Though all the fluorescence spectra have been scanned upto the other spectral extreme, *i.e.*, 800 nm of the instrument, the noticeable fluorescence could be recorded in the spectral region 450-650 nm only, which appears in the form of several humps superimposed on the broad tail of the excitation peak.

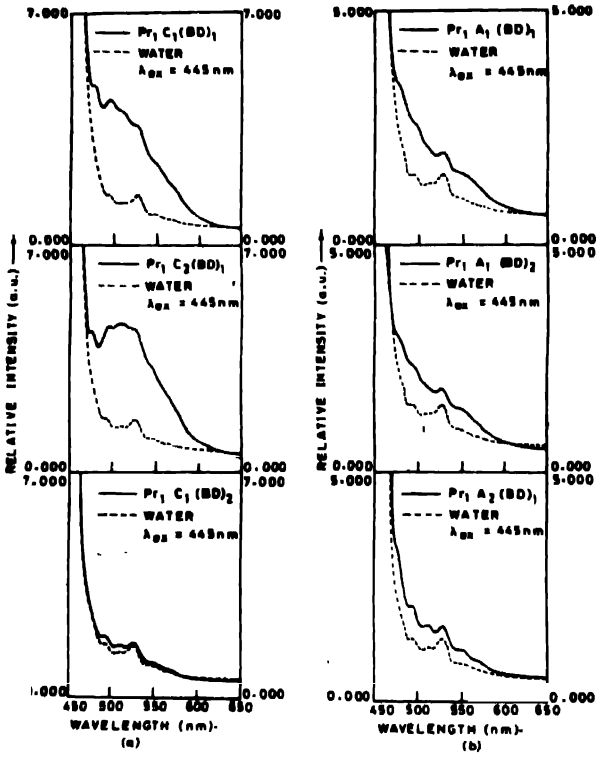

Figure 1. Fluorescence spectra of praseodymium ternary amino acid complexes in aqueous state.

Faint fluorescence peaks have been observed in the solvent spectrum which could be attributed to the fluorescent impurities (in ppm) left even after triple distillation. The spectra of solution and solvent contain almost coinciding fluorescence humps. However, their intensities differ considerably in the two spectra producing an evidence of hidden major fluorescence band. Interestingly in the case of $Pr_1 C_2 (BD)_1$complex (Figure 1(a)) this hidden band is resolved to a greater extent thus strengthening our presumption. For a better explanation of these observations, assistance has been sought from the work performed [10]

on similar complexes by our group, in which all the four absorption bands (444, 469, 482 and 590 nm) were employed for excitation, but only one broad fluorescence band centered at around 494 nm was observed in all cases, which on energy consideration has been assigned to the transition $^3P_0 \rightarrow {}^3H_4$. Further, the intensity of this band has been found to be maximum when excited by λ_{ex} = 444 nm $\left({}^3H_4 \rightarrow {}^3P_2\right)$. In order to test the effect of concentration on fluorescence quenching, three different concentrations, *viz.*, 0.01 M, 0.05 M and 0.10 M were investigated. It was observed [10] that the fluorescence quenching increases with the increase in concentration. Taking the above facts into consideration the main cause of the supressed fluorescence observed in the present course of investigation could be anticipated as the high concentration of the Pr^{3+} ions, which is as many as ten times higher than that used in other complexes [10] to record the noticeable fluorescence.

At higher concentrations, a large part of the excitation energy absorbed by the complex molecule is lost mainly through ion-ion interactions [11-14] and intermolecular exchanges [15,16,7]. This results in the decreased population of ions decaying radiatively from the fluorescing state which in its turn produces a weak fluorescence. Last but not the least, the effect of the solvent cannot be ignored as well, since hydrogen bonding and –OH group cause the dissipation of excitation energy non-radiatively. This fact is supported by the observation of high fluorescence intensity in aprotic solvents [17] which do not contain such groups.

Sm^{3+} complexes :

Four fluorescence bands each with an average and extreme peak fluorescence wavelength of 561.1±0.3, 596.6±0.4, 643.1±0.5 and 706.1±1.1 nm (Table 1) have been observed in case of all the six Sm^{3+} complexes.

Table 1. Fluorescence peak values (λ_p) and intensity values [I] for Sm^{3+} complexes monitored at the exciting radiation λ_{ex} = 401 nm $\left({}^6H_{5/2} \rightarrow {}^6P_{3/2}\right)$.

Transition →	$^4G_{5/2} \rightarrow {}^6H_{5/2}$		$^4G_{5/2} \rightarrow {}^6H_{7/2}$		$^4G_{5/2} \rightarrow {}^6H_{9/2}$		$^4G_{5/2} \rightarrow {}^6H_{11/2}$	
Complex ↓	λ_p (nm)	I (a.u.)	λ_p (nm)	I (a.u.)	λ_p (nm)	I (a.u.)	λ_p (nm)	I (a.u.)
$Sm_1A_1(BD)_1$	561.0	0.64	596.4	0.94	643.6	0.11	707.0	0.029
$Sm_1A_2(BD)_1$	561.4	1.02	597.0	1.57	642.8	0.24	707.2	0.053
$Sm_1A_1(BD)_2$	561.2	0.92	596.6	1.38	643.2	0.20	705.8	0.023
$Sm_1C_1(BD)_1$	560.8	0.97	596.2	1.30	642.6	0.17	705.4	0.044
$Sm_1C_1(BD)_2$	561.2	0.76	596.4	1.10	643.2	0.14	705.2	0.038
$Sm_1C_2(BD)_1$	561.2	1.01	596.6	1.51	642.6	0.22	705.0	0.042

On energy consideration, these bands have been assigned to the transitions initiating from the excited state $^4G_{5/2}$ and terminating at the ^6H manifolds, *viz.*, $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ respectively. These spectra have been recorded by scanning a single excitation wavelength, λ_{ex} = 401 nm, over the emission region 410–800 nm. However, for a better insight of the

fluorescence bands, only the relevant portion, *i.e.* 525–750 nm has been presented in Figure 2. The specific λ_{ex} (401 nm) was selected on the merit that it is the peak position of the most intense absorption band $\left({}^6H_{5/2} \rightarrow {}^6P_{3/2}\right)$.

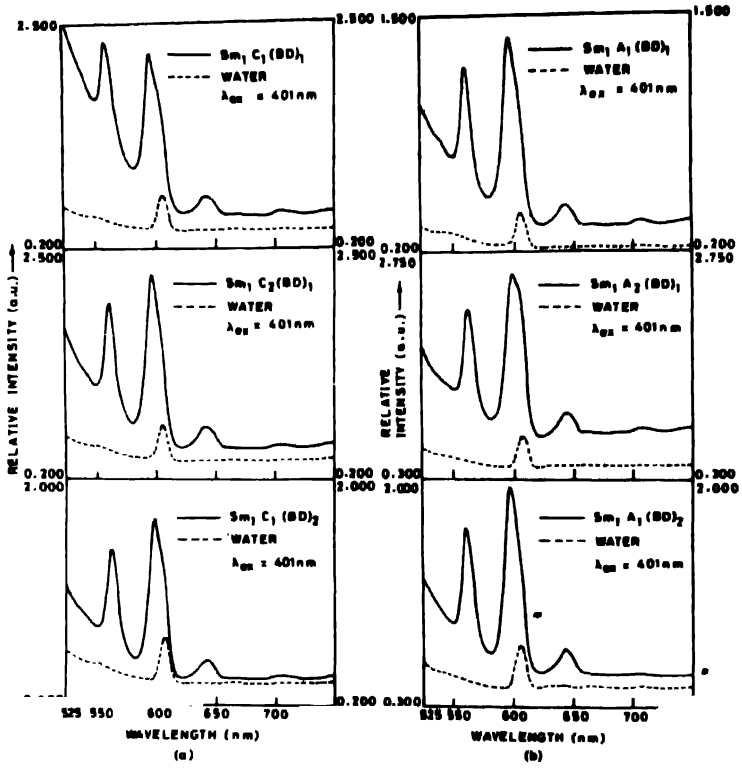

Figure 2. Fluorescence spectra of samarium ternary amino acid complexes in aqueous state.

It is interesting to note that certain fluorescent impurities in ppm concentration in the solvent have been found to be neutral to λ_{ex} = 401 nm in the present case which, however, played a villain role in the case of Pr^{3+} complexes (λ_{ex} = 445 nm). No significant interference from the solvent spectra other than Raman scattering has been observed in the solution spectra, thus making it possible to identify even a very faint fluorescence band due to the transition *viz.*, ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$.

The relative intensities alongwith the peak fluorescence wavelength (λ_p) for all the six complexes have been collected in Table 1. The intensity of the fluorescence band due to the transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$, appearing in the above table was corrected for Raman scattering prior to its inclusion in this table. This practice is essential for a more comprehensive comparison of the fluorescence intensities. A comparison among the fluorescence intensities of various transitions yields the following order :

$$ {}^4G_{5/2} \rightarrow {}^6H_{11/2} < {}^4G_{5/2} \rightarrow {}^6H_{9/2} < {}^4G_{5/2} \rightarrow {}^6H_{5/2} < {}^4G_{5/2} \rightarrow {}^6H_{7/2}. $$

This indicates that most of the excited ions try to approach more stabilized electronic state of the ^6H manifolds, thus resulting in the increased population of the ^6H manifolds with decreasing angular momentum. However, the lowest electronic state of this manifold, *i.e.*, ground state $^6H_{5/2}$, forms an exception with a reduction in its population as compared to $^6H_{7/2}$ state. This could most probably be attributed to the 'resonance' nature of this transition where the absorption process is being performed simultaneously towards higher energy side at an average and extreme spectral separations of 47 ± 16 cm^{-1} in general and of 59 and 42 cm^{-1} specifically for alanine and cysteine co-ordinated complexes respectively. This paves way to feed back some of the two grounded ions direct to the fluorescing state $^4G_{5/2}$, resulting in the decreased intensity of the fluorescence band due to transition $^4G_{5/2} \rightarrow {}^6H_{5/2}$.

Yet another comparison of fluorescence intensity of all the observed transition among different complexes yield the following order :

$$Sm_1 A_2 (BD)_1 > Sm_1 A_1 (BD)_2 > Sm_1 A_1 (BD)_1$$

for alanine co-ordinated complexes and

$$Sm_1 C_2 (BD)_1 > Sm_1 C_1 (BD)_1 > Sm_1 C_1 (BD)_2$$

for cysteine co-ordinated complexes. The linear nature of variation in intensity of all the transitions in these complexes indicates the similar mechanism of de-excitation.

Our results for fluorescence peaks at around 561 and 596 nm are found to be in a reasonable agreement with those for nitrogen donor ligand complexes [18,19]. However, they differ from those of benzoic acid complexes and its derivatives [20], where the possibility of the transfer of an electron from the organic part of the Sm^{3+} ion is anticipated [21], reducing it to the Sm^{2+} state.

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